

Particulate composition comprising dye fixatives

The present invention relates to a method of reducing dye loss or dye transfer from textile fibre materials, especially in the household sector, and to the particulate compositions used in that method, especially granules, comprising a dye fixative and a carrier, and to washing and softener compositions comprising such granules.

In customary household washing methods, dye loss when washing coloured textiles is a known problem. A further problem in that context is the transfer of dye when washing coloured textiles together with coloured or white textiles, especially with pale-coloured or white textiles.

The use of dye fixatives in textile care is known from WO 01/72982, which describes textile care products that comprise at least one cellulase and a dye-fixing basic polymer.

EP-A-692 511 discloses a method according to which fibre materials are dyed on an industrial scale and then treated with a dye fixative, the basic polycondensation product mentioned below, wherein the polycondensation product has not, however, been neutralised with an acid.

A problem with dye-fixing polymers is that they are deactivated in washing formulations that comprise anionic surfactants and are therefore no longer available for the intended use, namely the reduction of dye loss or dye transfer from textile materials.

The object of the present invention is to provide an improved method, suitable for the household sector, by means of which dye loss and/or dye transfer can be reduced further, and to provide washing formulations suitable for that method.

It has now been found, surprisingly, that the mentioned objective can be met to a great extent by means of particulate compositions comprising a dye fixative and a carrier.

The present invention accordingly relates to a method of reducing dye loss or dye transfer from textile fibre materials, especially in the household sector, in which method the textile fibre materials are treated with a particulate composition, especially granules, comprising

- a) from 1 to 90 % by weight of at least one water-soluble dye fixative,

- b) from 2 to 80 % by weight of at least one carrier,
 - c) from 0 to 60 % by weight of at least one binder that is soluble/dispersible in water,
 - d) from 0 to 20 % by weight of at least one further additive, and
 - e) from 0 to 15 % by weight water,
- the percentages in each case denoting percent by weight, based on the total weight of the composition.

The particulate compositions are preferably granules.

The particulate compositions are not glassy particles.

The particulate compositions can be used especially as a constituent in a washing composition and in washing composition additives or additive concentrates, e.g. pre- and/or after-treatment agents, stain-treatment salt, washing power enhancers, softeners, bleaching agents, UV protection enhancers, etc. in conventional concentrations. Such formulations can be present in all known and customary forms, especially in the form of powders, (super) compact powders, in the form of a single- or multi-layer tablet ("tabs"), bars, blocks, sheets, pastes, including in the form of pastes, gels or liquids which are used in capsules or in bags (sachets).

Powders can also be used in suitable sachets or bags.

Suitable dye fixatives a) are anionic, non-ionic or cationic compounds, especially cationic compounds, such as those disclosed, for example, in EP-A-692 511; or dye-fixing polymers, as disclosed, for example, in WO 01/74982. Dye-fixing polymers in the context of the present invention are to be understood as including, in addition to polymers, also oligomers and mixtures of oligomers and polymers.

Examples of dye fixatives are polydiallyldimethylammonium compounds, especially salts thereof and/or copolymers thereof, for example with polyacrylate, polyacrylamide and polyvinylpyrrolidone. Some of those compounds are obtainable from CIBA SC under the names Agefloc®, such as Agefloc C 505®, Agefloc WT40®, Agefloc WT40 SV® and Agefloc WT40 SVL®, or Agequat®, such as Agequat 3204®, Alcofix®, such as Alcofix R®, or Tinofix FRD®, preferably Agefloc WT40®, Agefloc WT40 SV® and Agefloc WT40 SVL®;

also bischloromethylbiphenylpolyquats, as described in Patent Specifications DE 2 657 582 and EP 225 281;

and polyethyleneimines obtainable from BASF under the name Lupasol[®], such as Lupasol SK[®], Lupasol PS[®], Lupasol FC[®], Lupasol WF[®], Lupasol P[®], Lupasol G20[®], anhydrous Lupasol G20[®], Lupasol G 100[®], Lupasol HF[®], Lupasol PR8515[®] and Lupasol FG[®], and preferably Lupasol G 100[®], Lupasol HF[®], Lupasol PR8515[®] and Lupasol FG[®], and Cyclanon[®];

further dye fixatives are, for example, basic polycondensation products containing imidazoline units, as described in WO 01/74982, or

Tinofix CL[®], Tinofix ULC[®], Tinofix ECO[®], Cibafix ECO[®] and Solfix E[®], which are obtainable from CIBA SC;

also Levogen FL[®], Levogen WSR[®], Levogen WRD[®] and Lavafix[®], which are obtainable from Bayer;

Gafquat 755N[®], Gafquat HS-100[®], Copolymer 845[®], Copolymer 958[®], Copolymer VC-713[®], Chromobond S-100[®] which is obtainable from ISP;

and also Neofix RE[®], Neofix E-225[®], Neofix E-117[®], Neofix RPA[®], Neofix F[®], Neofix RP-70[®] and Neofix R-250[®], which are obtainable from Nicca;

also Sevofix SR[®], Sevofix FFK[®] and Sevofix NOF[®], which are obtainable from Textil Color;

and also Indosol E-50[®], Indosol CRR[®], Sandofix FFN[®], Solidogen FRZR[®], Sandofix TPS[®], Sandofix TPSR[®], Sandofix WE56R[®] and Sandofix SWE[®], which are obtainable from Clariant.

In a preferred variant of the method according to the invention, the textile fibre material is treated with a particulate composition, which is especially in the form of granules, that comprises a dye fixative selected from the group of the following dye fixatives:

polydiallyldimethylammonium compounds, especially polydiallyldimethylammonium salts, bischloromethylbiphenylpolyquat compounds, the compound polyethyleneimine and basic polycondensation products, preferably those containing imidazolidine units and more preferably Tinofix CL[®].

Preference is also given to the method according to the invention wherein textile fibre material is treated with a particulate composition, which is especially in the form of granules, that comprises a dye fixative that is a basic polycondensation product of an amine of formula



and a cyanamide,

wherein the mentioned polycondensation products either have not been neutralised with an acid or have been neutralised wholly or partially with an inorganic or organic acid,

R_1 , R_2 , R_3 and R_4 each independently of the others being hydrogen or alkyl unsubstituted or substituted by amino, hydroxy, cyano or by C_1 - C_4 alkoxy, and

A being alkylene unsubstituted or substituted or uninterrupted or interrupted by one or more hetero atoms.

A in formula (1) is preferably C_2 - C_{20} alkylene uninterrupted or interrupted by -O-, -S-, -NH- or by -N(C_1 - C_4 alkyl)- and/or unsubstituted or substituted by hydroxy, preferably C_2 - C_{20} alkylene interrupted one or more times by -NH-.

R_1 , R_2 , R_3 and R_4 are each independently of the others preferably hydrogen or C_1 - C_4 alkyl.

Examples of suitable compounds of formula (1) are 1,4-butanediamine, 1,6-hexanediamine, dipropylenetriamine, N-(2-aminoethyl)-1,3-propanediamine, N,N-bis(2-aminopropyl)methylamine, polyethylenimine or polyethylenepolyamines, such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentamethylenhexamine.

Preferred compounds of formula (1) are polyethylenepolyamines and especially diethylenetriamine. The number of repeating units of the monomers of formula (1) in the basic polycondensation products is, for example, from 4 to 100, especially from 4 to 50.

Suitable cyanamides are, for example, cyanamide, dicyandiamide, guanidine and biguanidine. Dicyandiamide is preferred.

The above-mentioned dye fixatives are known, for example, from EP-A-692 511 or WO 01/74982 and can be obtained according to the processes disclosed therein.

For example, an amine of formula (1) is reacted with an ammonium salt in the presence of a non-aqueous solvent and the resulting protonated product is reacted with a cyanamide at elevated temperature.

Suitable ammonium salts are, for example, ammonium salts of organic or inorganic acids, for example ammonium chloride, ammonium sulfate, ammonium carbonate, ammonium formate and ammonium acetate, especially ammonium chloride.

Suitable non-aqueous solvents are, for example, hydroxyl-group-containing solvents, such as e.g. ethylene glycol, 1,2- or 1,3-propylene glycol, butylene glycol, di-, tri- or tetra-ethylene glycol and ethers thereof, and polyethylene glycols having a molecular weight of, for example, from 600 to 5000, and mixtures thereof.

The amine of formula (1) and the ammonium salt are used, for example, in a molar ratio of from 1:0.1 to 1:2.5, preferably from 1:0.7 to 1:2. The amount of hydroxyl-group-containing solvent can vary within a wide range and is, for example, from 0.2 to 20 mol, preferably from 0.4 to 5 mol, per mol of compound of formula (1).

The reaction of the amine of formula (1) with the ammonium salt is carried out especially at elevated temperature, such as from 80 to 200°C, especially from 100 to 160°C. For example, the amine of formula (1) is introduced into the hydroxyl-group-containing solvent or solvent mixture and the ammonium compound is metered in; advantageously the reaction step is carried out under inert conditions, such as under a nitrogen atmosphere.

The resulting protonated product is then reacted with, for example, from 0.5 to 2 mol, preferably from 0.8 to 1.5 mol, of cyanamide per mol of starting compound of formula (1). That reaction is carried out, for example, in the presence of one or more of the above-mentioned hydroxyl-group-containing solvents at elevated temperature, which is, for example, from 80 to 250°C, especially from 140 to 220°C. The reaction products are generally melts, having basic properties, that are solid at room temperature and yield clear solutions in water.

Neutralisation with an inorganic or organic acid is carried out, for example, in an aqueous medium, the addition of the acid being carried out in such a manner that a pH of, for

example, from 2 to 12, especially from 3 to 10 and preferably from 4 to 8, is obtained. Special preference is given to an amount of acid that yields a pH of about 7.

Suitable inorganic or organic acids are, for example, mono- or poly-carboxylic acids, hydrochloric acid, phosphoric acid, sulfuric acid or a mixture of at least two such acids. Preference is given to organic acids.

Examples of organic acids that may be mentioned are oxalic acid, tartaric acid, acetic acid, propionic acid, succinic acid, maleic acid, citric acid, formic acid, gluconic acid, p-toluene-sulfonic acid, terephthalic acid, benzoic acid, phthalic acid, acrylic acid and polyacrylic acid. Of special interest are aliphatic carboxylic acids, especially those having a total number of from 1 to 12 carbon atoms. Preferred acids are aliphatic C₁-C₁₂-mono- or poly-carboxylic acids, and in the case of monocarboxylic acids especially those having a total number of at least 3 carbon atoms. Suitable substituents of carboxylic acids are, for example, hydroxy and amino, especially hydroxy. Also of interest are mixtures of the mentioned acids; by way of example, mention may be made of the mixture of maleic acid and propionic acid.

Special preference is given to aliphatic C₂-C₁₂polycarboxylic acids, especially aliphatic C₂-C₆polycarboxylic acids. Very special preference is given to hydroxy-substituted aliphatic C₂-C₆polycarboxylic acids.

Suitable carriers b) are, for example, those disclosed in EP-A-133 562, for example water-soluble inorganic and organic salts, which may be textile washing component constituents that are customary *per se*, but preferably without the salt-type surfactants. Such carriers are primarily the customary structural substances, or builder substances, of washing compositions, such as e.g. the alkali metal silicates, carbonates, bicarbonates and borates also known as washing alkalis, and the alkali metal polyphosphates. Also suitable are, however, alkali metal sulfates that are virtually inert in the washing process, such as e.g. sodium sulfate.

Organic salts that can be used as carriers include water-soluble salts, especially alkali metal salts, of di- and poly-carboxylic acids, such as e.g. adipic acid, glutaric acid, succinic acid, maleic acid, phthalic acid, mellitic acid and cyclohexanhexacarboxylic acid; of hydroxy-carboxylic acids, such as e.g. citric acid, tartaric acid and salicylic acid; of aminocarboxylic acids, such as e.g. nitrilotriacetic acid and ethylenediaminetetraacetic acid; the salts of

organic polyphosphonic acids, such as e.g. isohydroxyethanediphosphonic acid, aminotri-methylenetriphosphonic acid, ethyldiaminotetramethylenetetraphosphonic acid, and the salts of polymeric polycarboxylates, such as e.g. homo- and co-polymerisation products of acrylic acid, hydroxyacrylic acid, maleic acid, methylenemalonic acid, and the copolymerisation products of such acids with vinyl methyl ether or methacrylic acid.

A further class of suitable carriers includes finely divided organic solids that are capable of swelling in water and/or are partially water-soluble, and absorbent polymeric powders, granules, fibres or fabrics, for example of the types cellulose, starch, especially carboxymethyl starch, dextrans and appropriate guar and algal derivatives, and also polyester, polyethylene, polyacrylonitrile, lignin, wood flour and sawdust.

Finally, a third class of suitable carriers consists of mixtures of very finely dispersed inorganic compounds that are insoluble in water. These include bentonites, such as sodium montmorillonite, layered silicates, and kieselguhr, talc, kaolin, mica, fuller's earth, feldspar and cation-exchanging zeolites of type A and X and hydrosodalite that also have a builder action in the washing process and are accordingly also suitable as phosphate exchange substances. Especially suitable carriers are sodium aluminium silicates, and especially silicates having a cavity structure. Also suitable as carriers of that class, however, are non-cation-exchanging finely divided zeolites and zeolites of the above types that are already present in the calcium form and cation-exchanging and non-cation-exchanging X-ray-amorphous alkali aluminosilicates, and also clay minerals, especially from the group of kaolins and the group of montmorillonites, also known as smectites. The very finely dispersed inorganic carriers that are insoluble in water include also very finely dispersed metal oxides and metal hydroxides and mixed oxides of silicon, aluminium, magnesium, zinc and titanium. These include very finely divided silicic acids that can be prepared by precipitation or pyrogenically, which, also in a form in which they have been reacted with polyorganosiloxanes, can be a main constituent of silicone oils. Typical examples of suitable metal oxides are very finely dispersed magnesium oxide, titanium oxide, zinc oxide and aluminium oxide. Such compounds have excellent carrier properties because of their high specific surface area, with the result that relatively small amounts are sufficient for their use as carrier in the particulate composition according to the invention and thus, when used in the washing process, subsequent loading of the washing liquor therewith is avoided.

A further class of suitable carriers are formaldehyde-containing polymers or oligomers of monomeric units such as melamine and formaldehyde or urea and formaldehyde, or phenol-formaldehyde resins.

Suitable carriers are also aerosils, silicon dioxide, metal oxide or metal hydroxide powders, such as, for example, TiO_2 , ZnO , MgO , Al_2O_3 , $\text{Al}(\text{OH})_3$ and Fe_2O_3 .

Further suitable carriers are alkaline earth metal salts, for example a calcium halide, such as calcium chloride, calcium bromide and calcium fluoride, calcium sulfate, calcium acetate, magnesium chloride, magnesium bromide, magnesium fluoride, magnesium sulfate and magnesium acetate.

The carriers may be used individually or in the form of a mixture of two or more carriers.

The carriers are commercial compounds and, for example, are obtainable commercially under the following names:

| Name | Manufacturer | Chemistry |
|---|------------------------|---|
| Wessalith XD [®] | Degussa | zeolite |
| Advera 401P [®] | PQ Corp. | zeolite |
| Laundrosil DGA [®] | Südchemie | activated bentonite |
| CBV 901 [®] | Zeolyst Int. | zeolite H-SDUSY |
| CBV 2802 [®] | Zeolyst Int. | zeolite H-ZSM-5 |
| Pergopak M [®] | Martinswerk | condensation product of urea and formaldehyde |
| Tino Flow [®] | Ciba | |
| Arbocel FDY600 [®] , BC200 [®] , G350 [®] | J. Rettenmaier & Söhne | cellulose fibres |
| sodium chloride, sodium sulfate | Merck, Riedel | |

In a further preferred variant of the method according to the invention, the textile fibre material is treated with a particulate composition comprising a carrier that comprises at least one of the following components:

- a) water-soluble inorganic and/or organic salts, which may especially be customary textile washing composition constituents but are preferably not surfactant components,
- b) finely divided organic solids that are capable of swelling in water and/or are partially water-soluble, and
- c) very finely dispersed water-insoluble inorganic carriers.

In an especially preferred variant of the method according to the invention, the textile fibre material is treated with a particulate composition comprising a carrier selected from the group of the following carriers: zeolites, bentonites, kieselguhr, talc, kaolin, mica, fuller's earth, cellulose, feldspar and condensation products of urea and formaldehyde.

In the present invention binders c) are, for example, anionic dispersants, non-ionic surfactants and dispersants or water-soluble polymers, which are defined hereinbelow.

a) Anionic dispersants

The anionic dispersants used are, for example, commercially available water-soluble anionic dispersants for dyes and pigments.

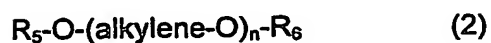
The following products in particular come into consideration: condensation products of aromatic sulfonic acids and formaldehyde, condensation products of aromatic sulfonic acids with optionally chlorinated diphenylene or diphenyl oxides and optionally formaldehyde, (mono-/di-)alkylnaphthalenesulfonates, sodium salts of polymerised organic sulfonic acids, sodium salts of polymerised alkylnaphthalenesulfonic acid, sodium salts of polymerised alkylbenzenesulfonic acids, alkylarylsulfonates, sodium salts of alkylpolyglycol ether sulfates, polyalkylated polynuclear arylsulfonates, methylene-linked condensation products of aryl-sulfonic acids and hydroxyarylsulfonic acids, sodium salts of dialkylsulfosuccinic acids, sodium salts of alkyldiglycol ether sulfates, sodium salts of polynaphthalenemethanesulfonates, lignin sulfonates or oxylignin sulfonates or heterocyclic polysulfonic acids.

b) Non-ionic surfactants and dispersants

Suitable non-ionic dispersants are especially compounds that are emulsifiable, dispersible or soluble in water, preferably having a melting point of at least 35°C. They are, for example, the following compounds:

1. fatty alcohols having from 8 to 22 carbon atoms, especially cetyl alcohol;
2. addition products of preferably from 2 to 80 mol of alkylene oxide, especially ethylene oxide, it being possible for individual ethylene oxide units to have been replaced by substituted epoxides, such as styrene oxide and/or propylene oxide, with higher unsaturated or saturated monoalcohols, fatty acids, fatty amines or fatty amides having from 8 to 22 carbon atoms, or with benzyl alcohols, phenylphenols, benzylphenols or alkylphenols, the alkyl radicals thereof having at least 4 carbon atoms;
3. condensation products of alkylene oxides, especially of propylene oxide (block polymerisation products);
4. ethylene oxide/propylene oxide adducts with diamines, especially ethylenediamine;
5. reaction products of a fatty acid having from 8 to 22 carbon atoms and a primary or secondary amine having at least one hydroxy-lower alkyl or lower alkoxy-lower alkyl group or alkylene oxide addition products of such hydroxyalkyl-group-containing reaction products;
6. sorbitan esters, preferably having long-chained ester groups, or ethoxylated sorbitan esters, such as e.g. polyoxyethylene sorbitan monolaurate having from 4 to 10 ethylene oxide units or polyoxyethylene sorbitan trioleate having from 4 to 20 ethylene oxide units,
7. addition products of propylene oxide with a tri- to hexa-hydric aliphatic alcohol having from 3 to 6 carbon atoms, e.g. glycerol or pentaerythritol; and
8. fatty alcohol polyglycol mixed ethers, especially addition products of from 3 to 30 mol of ethylene oxide and from 3 to 30 mol of propylene oxide with aliphatic monoalcohols having from 8 to 22 carbon atoms.

Especially suitable non-ionogenic dispersants are surfactants of formula



wherein

R_5 is C_8-C_{22} alkyl or C_8-C_{18} alkenyl;

R_6 is hydrogen; C_1-C_4 alkyl; a cycloaliphatic radical having at least 6 carbon atoms; or benzyl;

"alkylene" is an alkylene radical having from 2 to 4 carbon atoms, and

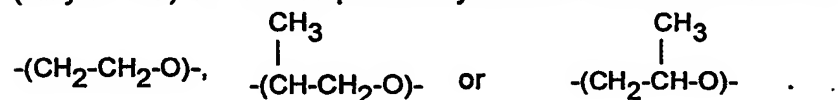
n is a number from 1 to 60.

The substituents R_5 and R_6 in formula (2) are advantageously the hydrocarbon radical of an unsaturated or preferably saturated aliphatic monoalcohol having from 8 to 22 carbon atoms. The hydrocarbon radical can be straight-chained or branched. Preferably R_5 and R_6 are each independently of the other an alkyl radical having from 9 to 14 carbon atoms.

Suitable aliphatic saturated monoalcohols are natural alcohols, for example lauryl alcohol, myristyl alcohol, cetyl alcohol or stearyl alcohol, and synthetic alcohols, for example 2-ethylhexanol, 1,1,3,3-tetramethylbutanol, octan-2-ol, isononyl alcohol, trimethylhexanol, trimethylnonyl alcohol, decanol, C_9 - C_{11} oxoalcohol, tridecyl alcohol, isotridecyl alcohol and linear primary alcohols (Alfol[®] products) having from 8 to 22 carbon atoms. Examples of such Alfol[®] products are Alfol[®] (8-10), Alfol[®] (9-11), Alfol[®] (10-14), Alfol[®] (12-13) and Alfol[®] (16-18). Unsaturated aliphatic monoalcohols are, for example, dodecenyl alcohol, hexadecenyl alcohol or oleyl alcohol.

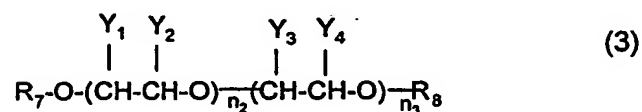
The alcohol radicals can be present individually or in the form of mixtures of two or more components, for example mixtures of alkyl and/or alkenyl groups derived from soybean fatty acids, palm kernel fatty acids or tallow oils.

(Alkylene-O) chains are preferably divalent radicals of formula



Examples of a cycloaliphatic radical are cycloheptyl, cyclooctyl or preferably cyclohexyl.

Suitable non-ionogenic dispersants are preferably surfactants of formula



wherein

R_7 is C_8 - C_{22} alkyl;

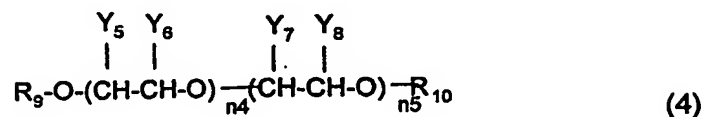
R_8 is hydrogen or C_1 - C_4 alkyl;

Y_1 , Y_2 , Y_3 and Y_4 are each independently of the others hydrogen, methyl or ethyl;

n_2 is a number from 0 to 8; and

n_3 is a number from 2 to 40.

Further important non-ionogenic dispersants correspond to formula



wherein

R_9 is $\text{C}_9\text{-C}_{14}$ alkyl;

R_{10} is $\text{C}_1\text{-C}_4$ alkyl;

Y_5 , Y_6 , Y_7 and Y_8 are each independently of the others hydrogen, methyl or ethyl, one of the radicals Y_5 and Y_6 and one of the radicals Y_7 and Y_8 always being hydrogen; and

n_4 and n_5 are each independently of the other an integer from 4 to 8.

The non-ionogenic dispersants of formulae (2) to (4) can be used in the form of mixtures. For example, suitable surfactant mixtures are non-end-group-terminated fatty alcohol ethoxylates of formula (2), that is to say compounds of formula (2) wherein

R_5 is $\text{C}_8\text{-C}_{22}$ alkyl,

R_6 is hydrogen and

the alkylene-O chain is the radical $\text{-(CH}_2\text{-CH}_2\text{-O)-}$,

and end-group-terminated fatty alcohol ethoxylates of formula (4).

Examples of the non-ionogenic dispersants of formulae (2), (3) and (4) that may be mentioned include reaction products of a $\text{C}_{10}\text{-C}_{13}$ fatty alcohol, e.g. of a C_{13} oxoalcohol, with from 3 to 10 mol of ethylene oxide, propylene oxide and/or butylene oxide or the reaction product of 1 mol of a C_{13} fatty alcohol with 6 mol of ethylene oxide and 1 mol of butylene oxide, it being possible for the addition products each to be end-group-terminated by $\text{C}_1\text{-C}_4$ alkyl, preferably methyl or butyl.

c) Water-soluble polymers

Suitable water-soluble organic polymers are, for example, sugars and sugar derivatives, such as cyclodextrins, polysaccharides (e.g. starch, maltodextrin), carboxymethylcellulose, hydroxymethylcellulose, alginates, polyaspartic acid, polyethylene glycols, ethylene oxide/-propylene oxide copolymers, gelatin, polyacrylates, polymethacrylates, polyvinylpyrrolidones, vinylpyrrolidones, vinyl acetates, copolymers of vinylpyrrolidone with long-chained α -olefins,

copolymers of styrene and acrylic acid, polycarboxylic acids, poly(vinylpyrrolidone/-dimethylaminoethyl methacrylates), copolymers of vinylpyrrolidone/dimethylaminopropylmethacrylamides, copolymers of vinylpyrrolidone/dimethylaminopropylacrylamides, quaternised copolymers of vinylpyrrolidones and dimethylaminoethyl methacrylates, terpolymers of vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of vinylpyrrolidone and methacrylamidopropyltrimethylammonium chloride, terpolymers of caprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, polyacrylamides, polyvinyl alcohols, optionally hydrolysed polyvinyl acetate, copolymers of ethyl acrylate with methacrylate and methacrylic acid, copolymers of maleic acid with unsaturated hydrocarbons and mixed polymerisation products of the mentioned polymers.

In a preferred embodiment of the composition according to the invention, non-ionic dispersants and/or water-soluble polymers are used as binders. Special preference is given to starch, maltodextrin and carboxymethylcellulose, hydroxymethylcellulose, polyethylene glycols, ethylene oxide/propylene oxide copolymers, polyvinyl alcohols and gelatin.

The particulate compositions according to the invention may comprise further additives, for example wetting agents, water-insoluble or water-soluble dyes, fillers, pigments, perfume oils, foam-regulators, thickeners, microbicides, complexing agents, dissolution accelerators and fluorescent whitening agents, UV absorbers, antioxidants or anti-dust agents.

The particulate compositions, which are especially granules, can also be prepared in such a manner that they are in the form of coated particles or granules. Suitable coating materials, in addition to the conventional substances mentioned in connection with the binders, are, for example, polymethacrylic acid, polyethylenesulfonic acids, polystyrenesulfonic acids, copolymers of acrylic acid with sulfonated styrenes, gum arabic, hydroxypropylcellulose, hydroxymethylpropylcellulose or the phthalate thereof, and waxy substances, such as e.g. glyceryl monostearate, glyceryl distearate, beeswax, waxy paraffins, stearic acid or the magnesium or calcium salts thereof. Such additives are present in an amount of from 0 to 20 % by weight, based on the total weight of the particulate compositions.

The particulate compositions according to the invention, which are especially granules, may also be uncoated and have a substantially homogeneous distribution of their constituents.

The particulate compositions according to the invention also comprise from 0 to 15 % by weight water.

The particulate compositions according to the invention, especially granules, are prepared in various ways starting from liquid or solid dye fixative, by

- a) dissolving a dye fixative or a dye fixative and a binder, and then bringing a solid carrier into contact with the solution, preferably forming a suspension therein, or
- b) dissolving a dye fixative or a dye fixative and a binder, and then applying the solution to the solid carrier or granulating it therewith, or
- c) extruding a paste comprising a dye fixative, a carrier and a binder, or
- d) granulating a mixture consisting of a dye fixative, a carrier and possibly a binder, by spray application of a solvent or a melt in which further binders may have been dissolved, and drying the compositions obtained according to methods a), b), c) or d), or allowing them to solidify by cooling. Coating of the resulting granules can also be carried out, for example, by, in a subsequent step, spraying the granules with a solution of a coating material and drying them or coating them with a melt.

In respect of method a):

First the active ingredient, the binder and optionally further additives are dissolved in water and the mixture is stirred, optionally with heating, until a homogeneous solution is obtained. The carrier material is then suspended in that aqueous solution. The mixture is stirred until a homogeneous suspension is obtained. The solids content of the suspension should preferably be at least 30 % by weight, especially from 40 to 50 % by weight, based on the total weight of the solution. The viscosity of the solution is preferably less than 1500 mPas.

In a drying step all the water except for a residual amount is then removed from the aqueous suspension prepared in that manner, solid particles, for example granules, being formed at the same time.

Generally known processes are suitable for preparing the granules from the aqueous suspension. In principle, processes involving a continuous procedure and also processes involving a discontinuous procedure are suitable. Preference is given to the use of continuous processes, especially spray-drying and fluidised bed granulating processes.

Especially suitable are spray-drying processes in which the active ingredient solution is sprayed into a chamber with circulating hot air. Atomisation of the solution is effected by

means of unitary or binary nozzles or by the spin effect of a rapidly rotating disk. In order to increase the size of the particles, the spray-drying process can be combined with additional agglomeration of the liquid particles with solid seeds in a fluidised bed incorporated into the chamber (so-called fluid spray). The fine particles ($< 100 \mu\text{m}$) resulting from a conventional spray-drying process can be fed, optionally after being separated out from the discharge gas stream, as seed, without further treatment directly into the spray cone of the atomiser of the spray-dryer to achieve agglomeration with the liquid drops of the active ingredient.

During the granulation step, water can be removed rapidly from the suspensions comprising the carrier and the dye fixative, and agglomeration of the drops forming in the spray cone or of drops with solids particles is expressly intended.

If required, the granules formed in the spray-dryer are separated out in a continuous process, for example by a screening procedure. In that process, the fines and oversize material are either recycled directly (without intermediate dissolution) or suspended in the liquid active ingredient formulation and then granulated again.

In respect of method b):

First a solution consisting of dissolved dye fixative and optionally further binders and additives is prepared. The solution is then applied to the carrier in a granulator by means of a spray device, granules being formed by agglomeration. The granulation is effected either in a batch process or in a continuous procedure. Suitable granulators are fluidised bed granulators or horizontally or vertically rotating mixers. When the granulation process is complete, the water is removed from the granules with the exception of the desired residual amount. This is effected either in the same apparatus or in a separate after-dryer.

In respect of method c):

A paste consisting of a dye fixative, carrier and optionally a binder is prepared in a kneading apparatus. The components are made into a paste either by the addition of a suitable amount of water or by melting one or more of the formulation components. The paste is then fed into an extruder and shaped into cylindrical particles (diameter 0.5 - 2 mm, length 1 - 3 mm; ratio of diameter/length from 1:1 to 1:4). The extruded material is dried/solidified in a further step. If desired, the extruded material can be rounded off in a separate step. Any fines produced are recycled in the process.

In respect of method d):

A homogeneous dry mixture consisting of a dye fixative, carrier and binder is prepared in a mixer. The mixture is then granulated in a granulator with spray application of a molten binder, an aqueous binder solution or, where appropriate, water alone. The granulation is effected either in a batch process or continuously. Suitable granulators are both fluidised bed granulators and horizontally or vertically rotating mixers. When the granulation process is complete, water is removed from the granules with the exception of the desired residual amount, or in the case of molten binder, the granules solidify.

The granules according to the invention are resistant to abrasion, low in dust, free-flowing and easily meterable. They are distinguished by a rate of dissolution in water that can be controlled by means of the composition of the formulation.

The dye fixative content of the granules is from 1 to 90 % by weight, preferably from 5 to 88 % by weight, especially from 10 to 78 % by weight. The size of the granules can be matched to suit the target product and is from 0.05 mm to 4 mm, preferably from 0.1 mm to 2 mm.

Accordingly, the present invention relates also to the above-defined particulate compositions, especially granules, comprising

- a) from 1 to 90 % by weight of at least one water-soluble dye fixative,
- b) from 2 to 80 % by weight of at least one carrier,
- c) from 0 to 60 % by weight of at least one binder that is soluble/dispersible in water,
- d) from 0 to 20 % by weight of at least one further additive, and
- e) from 0 to 15 % by weight water,

the percentages in each case denoting percent by weight, based on the total weight of the composition.

All the definitions and preferred meanings mentioned above for the method according to the invention apply also to the particulate compositions according to the invention.

Preferred particulate compositions according to the invention are granules.

Further preferred particulate compositions according to the invention, especially granules, consist of

a) from 1 to 90 % by weight of at least one basic polycondensation product of an amine of formula



and a cyanamide, wherein the mentioned polycondensation product either has not been neutralised or has been neutralised wholly or partially with an inorganic or organic acid, R_1 , R_2 , R_3 and R_4 each independently of the others being hydrogen or alkyl unsubstituted or substituted by amino, hydroxy, cyano or by C_1 - C_4 alkoxy, and A being alkylene unsubstituted or substituted or uninterrupted or interrupted by one or more hetero atoms,

b) from 2 to 80 % by weight of at least one carrier from the group consisting of zeolites, bentonites, kieselguhr, talc, kaolin, mica, fuller's earth, cellulose, feldspar and/or condensation products of urea and formaldehyde,

c) from 0 to 60 % by weight of at least one compound from the group consisting of starch, maltodextrin and carboxymethylcellulose, hydroxymethylcellulose, polyethylene glycols, ethylene oxide/propylene oxide copolymers, polyvinyl alcohols and/or gelatin,

d) from 0 to 20 % by weight of at least one further additive from the group consisting of wetting agents, water-insoluble or water-soluble dyes, fillers, pigments, perfume oils, foam-regulators, thickeners, microbicides, complexing agents, dissolution accelerators, fluorescent whitening agents, UV absorbers, antioxidants and/or anti-dust agents, and

e) from 0 to 15 % by weight water,

the percentages in each case denoting percent by weight, based on the total weight of the composition.

Still greater preference is given to particulate compositions according to the invention wherein A in formula (1) of the dye fixative is C_2 - C_{20} alkylene uninterrupted or interrupted by -O-, -S-, -NH- or by -N(C_1 - C_4 alkyl) and/or unsubstituted or substituted by hydroxy, preferably C_2 - C_{20} alkylene interrupted one or more times by -NH-.

Especially preferred particulate compositions according to the invention are those wherein the compound of formula (1) is a polyethylenepolyamine, especially diethylenetriamine.

Especially preferred particulate compositions according to the invention are also those wherein the cyanamide is dicyandiamide.

Especially preferred particulate compositions according to the invention are also those wherein the inorganic or organic acid is a mono- or poly-carboxylic acid, hydrochloric acid, phosphoric acid, sulfuric acid or a mixture of at least two such acids.

Depending on the composition of the granules according to the invention, the formulations according to the invention may also be used as an additive in other formulations or in combination with another formulation. The preferred use of the formulations according to the invention is use in a washing composition or in a washing composition additive, for example in pre- and/or after-treatment agents, in stain-treatment salts, in washing power enhancers, in softeners, in bleaching agents or in UV protection enhancers.

The formulations according to the invention are used especially as an additive in a washing formulation. Such a washing formulation may be in solid, liquid, gel-like or pasty form, for example in the form of a liquid, non-aqueous washing composition comprising not more than 5 % by weight, preferably from 0 to 1 % by weight, water, and may be based on a suspension of a builder substance in a non-ionic surfactant, for example as described in GB-A-2 158 454.

The formulation according to the invention may also be in the form of a powder, a (super) compact powder, a single- or multi-layer tablet (tabs), in the form of washing composition bars, washing composition blocks, washing composition sheets, washing composition pastes, washing composition gels, also in the form of powders, pastes, gels or liquids which are used in capsules or in bags (sachets).

However, the washing compositions are preferably in the form of non-aqueous formulations, powders, tabs or granules.

The present invention accordingly relates also to washing formulations comprising
I) 5 - 90 % of A) at least one anionic surfactant and/or B) at least one
non-ionic surfactant, based on the total weight of the
washing formulation,

- II) 5 - 70 % of C) at least one builder substance, based on the total weight of the washing formulation,
- III) 0 - 30 % of D) at least one peroxide and optionally at least one activator, based on the total weight of the washing formulation,
- IV) 0.1 - 70 % of E) at least one particulate composition comprising
 - a) from 1 to 90 % by weight of at least one water-soluble dye fixative,
 - b) from 2 to 80 % by weight of at least one carrier,
 - c) from 0 to 60 % by weight of at least one binder that is soluble/dispersible in water,
 - d) from 0 to 20 % by weight of at least one further additive, and
 - e) from 0 to 15 % by weight of water,
- V) 0 - 60 % of F) at least one further additive, and
- VI) 0 - 12 % of G) water.

The present invention accordingly preferably relates also to washing formulations comprising

- I) 5 - 70 % of A) at least one anionic surfactant and/or B) at least one non-ionic surfactant, based on the total weight of the washing formulation,
- II) 5 - 50 %, preferably 5 - 40 % by weight, of C) at least one builder substance, based on the total weight of the washing formulation,
- III) 0 - 12 % of D) at least one peroxide and optionally at least preferably from 5 to 40 % by weight of an activator, based on the total weight of the washing formulation, and
- IV) 0.2 - 50 %, preferably from 0.3 - 40 % by weight, of E) at least one particulate composition comprising
 - a) from 1 to 90 % by weight of at least one water-soluble dye fixative,
 - b) from 2 to 80 % by weight of at least one carrier,
 - c) from 0 to 60 % by weight of at least one binder that is soluble/dispersible in water,
 - d) from 0 to 20 % by weight of at least one further additive, and
 - e) from 0 to 15 % by weight of water,
- V) 0 - 60 % of F) at least one further additive, and
- VI) 0 - 12 % of G) water.

The sum of the percent by weight of components I) to VI) in a formulation is always 100 %.

For the particulate composition in E), the preferences mentioned above apply in respect of constituents a) to e).

The anionic surfactant A) may be, for example, a sulfate, sulfonate or carboxylate surfactant or a mixture thereof. Preferred sulfates are those having from 12 to 22 carbon atoms in the alkyl moiety or alkylethoxy sulfates in which the alkyl moiety has from 10 to 20 carbon atoms and the head group possesses on average 2 or 3 ethoxy units. Preferred sulfonates are, for example, alkylbenzenesulfonates having from 9 to 15 carbon atoms in the alkyl moiety and/or alkylnaphthalenesulfonates having from 6 to 16 carbon atoms in the respective alkyl moiety. The cation in the case of the anionic surfactants is preferably an alkali metal cation, especially sodium. Preferred carboxylates are alkali metal sarcosinates of the formula $R_{11}-CO-N(R_{12})-CH_2COOM^1$, wherein R_{11} is alkyl or alkenyl having from 8 to 18 carbon atoms in the alkyl or alkenyl moiety, R_{12} is C_1 - C_4 alkyl and M^1 is an alkali metal.

The non-ionic surfactant B) may be, for example, a condensation product of from 3 to 8 mol of ethylene oxide with 1 mol of primary alcohol having from 9 to 15 carbon atoms.

Suitable builder substances C) are, for example, alkali metal phosphates, especially tripolyphosphates, carbonates or bicarbonates, especially the sodium salts thereof, silicates, aluminium silicates, polycarboxylates, polycarboxylic acids, organic phosphonates, aminoalkylenepoly-(alkylene phosphonates) or mixtures of those compounds. Especially suitable silicates are the sodium salts of crystalline layered silicates of the formula $NaHSi_tO_{2t+1}.pH_2O$ or $Na_2Si_tO_{2t+1}.pH_2O$, wherein t is a number from 1.9 to 4 and p is a number from 0 to 20. Of the aluminium silicates, preference is given to those which are available commercially under the names Zeolite A, B, X and HS, as well as mixtures containing two or more of those components.

Of the polycarboxylates, preference is given to the polyhydroxy carboxylates, especially citrates, and acrylates and copolymers thereof with maleic anhydride. Preferred polycarboxylic acids are nitrilotriacetic acid, ethylenediaminetetraacetic acid as well as ethylenediamine disuccinate both in racemic form and in the enantiomerically pure S,S form. Especially suitable phosphonates or aminoalkylenepoly(alkylene phosphonates) are alkali metal salts of 1-hydroxyethane-1,1-diphosphonic acid, nitrilotris(methylenephosphonic acid), ethylenediamine-tetramethylenephosphonic acid and diethylenetriaminepenta-methylenephosphonic acid.

Suitable as the peroxide component D) are, for example, the commercially available organic and inorganic peroxides known from the literature, which bleach textile materials at customary washing temperatures, for example from 10 to 95°C. The organic peroxides are, for example, mono- or poly-peroxides, especially organic per-acids or salts thereof, such as phthalimidoperoxyacaproic acid, peroxybenzoic acid, diperoxydodecanedioic acid, diperoxy-nonanedioic acid, diperoxydecanedioic acid, diperoxyphthalic acid or salts thereof. Preference is given, however, to the use of inorganic peroxides, for example persulfates, perborates, percarbonates and/or persilicates. Of course it is also possible to use mixtures of inorganic and/or organic peroxides. The peroxides may be present in various crystalline forms and may have different water contents and can also be used together with other inorganic or organic compounds in order to improve their storage stability. The addition of the peroxides to the washing composition is preferably carried out by mixing the components, for example by means of a screw metering system and/or a fluidised bed mixer.

In addition to the combination according to the invention, the washing compositions can also comprise one or more fluorescent whitening agents, for example from the class bis-triazinylamino-stilbene-disulfonic acid, bis-triazolyl-stilbene-disulfonic acid, bis-styryl-biphenyl or bis-benzofuranyl-biphenyl, a bis-benzoxalyl derivative, a bis-benzimidazolyl derivative, a coumarin derivative or a pyrazoline derivative.

The washing compositions may also comprise suspending agents for dirt, e.g. sodium carboxymethylcellulose, pH regulators, e.g. alkali metal or alkaline earth metal silicates, foam-regulators, e.g. soap, salts for regulating spray-drying and granulating properties, e.g. sodium sulfate, fragrances and, optionally, antistatics and softeners, enzymes, such as amylase, bleaching agents, pigments and/or toning agents. Such constituents must, of course, be stable towards the bleaching agent used.

The washing formulation may additionally comprise further polymers which during the washing of textiles prevent staining by dyes found in the washing liquor which have dissolved out of the textiles under the washing conditions.

In addition, the washing compositions according to the invention may also comprise so-called perborate activators, e.g. TAED or TAGU. Preference is given to TAED, which is preferably used in an amount of from 0.05 to 5 % by weight, especially from 0.2 to 1.7 % by weight, based on the total weight of the washing composition.

The percentages of components I) to VI) in the following washing formulations are always based on the total weight of the washing formulation.

A preferred washing formulation according to the invention consists of

I) 5 - 90 %

of A) at least one anionic surfactant from the group consisting of C₁₂-C₂₂alkylethoxysulfates in which the alkyl moiety has from 10 to 20 carbon atoms and the head group contains on average 2 or 3 ethoxy units; alkylbenzenesulfonates having from 9 to 15 carbon atoms in the alkyl moiety; alkylnaphthalenesulfonates having from 6 to 16 carbon atoms in the respective alkyl moiety; or alkali metal sarcosinates of the formula R₁₁-CO-N(R₁₂)-CH₂COOM₁, wherein R₁₁ is alkyl or alkenyl having from 8 to 18 carbon atoms in the alkyl or alkenyl moiety, R₁₂ is C₁-C₄alkyl and M₁ is an alkali metal, and/or

B) at least one non-ionic surfactant from the group consisting of a condensation product of from 3 to 8 mol of ethylene oxide with 1 mol of primary alcohol having from 9 to 15 carbon atoms,

II) 5 - 70 %

of C) a builder substance from the group consisting of alkali metal phosphates; carbonates; bicarbonates; silicates; aluminium silicates; polycarboxylates; polycarboxylic acids; organic phosphonates or aminoalkylenepoly-(alkylene phosphonates),

III) 0 - 30 %

of D) a peroxide from the group consisting of organic mono- or poly-peroxides; organic per-acids or salts thereof; persulfates; perborates; percarbonates; persilicates,

IV) 0.1 - 70 %

of E) granules comprising

a) from 1 to 90 % by weight, preferably from 5 to 88 % by weight, especially from 10 to 78 % by weight, of polydiallyldimethylammonium compounds, especially polydiallyldimethylammonium salts, bischloromethylbiphenylpolyquat compounds, the compound polyethyleneimine and basic polycondensation products,

preferably those containing imidazolidine units and especially Tinofix CL[®],

- b) from 2 to 80 % by weight of at least one carrier from the group consisting of zeolites, bentonites, kieselguhr, talc, kaolin, mica, fuller's earth, cellulose, feldspar and condensation products of urea and formaldehyde,
- c) from 0 to 60 % by weight of at least one non-ionic dispersant and/or water-soluble polymer from the group consisting of starch, maltodextrin and carboxymethylcellulose, hydroxymethylcellulose, polyethylene glycols, ethylene oxide/propylene oxide copolymers, polyvinyl alcohols and gelatin,
- d) from 0 to 20 % by weight of at least one further additive from the group consisting of wetting agents; disintegrators; fillers, water-insoluble or water-soluble dyes or pigments; dissolution accelerators; fluorescent whitening agents; aluminium silicates; powdered cellulose; fibrous cellulose; microcrystalline cellulose; talc; kaolin; TiO₂; SiO₂ and magnesium trisilicate, and
- e) from 0 to 15 % by weight water, in each case based on the total weight of the granules,

- V) 0 – 60 % of F) further additives from the group consisting of fluorescent whitening agents; suspending agents for dirt; pH regulators; foam-regulators; salts for regulating spray-drying and granulating properties; fragrances; antistatics; softeners; enzymes; bleaching agents; pigments; toning agents; further polymers which during the washing of textiles prevent staining by dyes found in the washing liquor which have dissolved out of the textiles under washing conditions; and bleaching agent activators, and
- VI) 0 – 12 % of G) water.

The present invention relates also to a softener composition for reducing dye loss or dye transfer from textile fibre materials, especially in the household sector, comprising a particulate composition that comprises a carrier and a dye fixative.

Preference is given to a softener composition comprising a particulate composition consisting of

- a) from 1 to 90 % by weight of a water-soluble dye fixative,
- b) from 2 to 80 % by weight of a carrier,
- c) from 0 to 60 % by weight of a binder that is soluble/dispersible in water,
- d) from 0 to 20 % by weight of a further additive, and
- e) from 0 to 15 % by weight water,

the percentages in each case denoting percent by weight, based on the total weight of the composition.

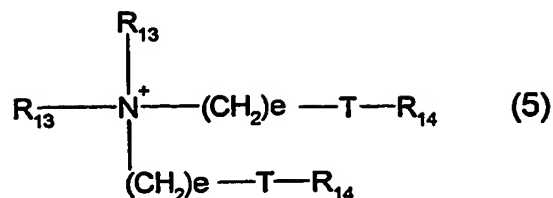
Softeners, especially hydrocarbon softeners, which can be used herein are selected especially from the following classes of compounds:

(i) Cationic quaternary ammonium salts. The counter-ion of such cationic quaternary ammonium salts may be a halide, for example chloride or bromide, dimethyl sulfate or other ions known from the literature. The counter-ion is preferably dimethyl sulfate or any desired alkyl sulfate or halide, with dimethyl sulfate being most preferred for the articles of this invention added to the dryer.

Examples of cationic quaternary ammonium salts include but are not limited to:

(1) Acyclic quaternary ammonium salts which contain at least two C_8 - C_{30} -, preferably C_{12} - C_{22} -alkyl or -alkenyl chains, for example:

ditallow dimethylammonium dimethyl sulfate, di(hydrogenated tallow) dimethylammonium dimethyl sulfate, di(hydrogenated tallow) dimethylammonium methyl chloride, distearyl-dimethylammonium dimethyl sulfate, dicocodimethylammonium dimethyl sulfate and the like. In particular, the textile softener compound is preferably a water-insoluble quaternary ammonium material that contains a compound having two C_{12} - C_{18} -alkyl- or -alkenyl groups bonded to the molecule by at least one ester bond. The presence of two ester bonds in the quaternary ammonium material is especially preferred. An especially preferred ester-bonded quaternary ammonium material for use in this invention can be represented by the following formula:



wherein

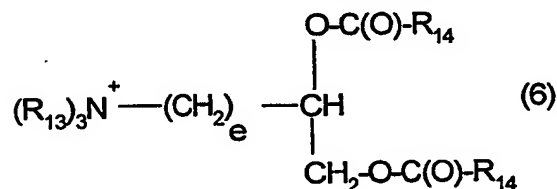
each group R_{13} is selected independently of the other from C_1 - C_4 alkyl, hydroxyalkyl or C_2 - C_4 -alkenyl groups;

T is either -O-C(O)- or -C(O)-O-, and wherein

each group R_{14} is selected independently of the other from C_8 - C_{28} alkyl or C_8 - C_{28} alkenyl groups; and

e is an integer from 0 to 5.

A second preferred type of quaternary ammonium can be represented by the formula:



wherein R_{13} , e and R_{14} are as defined above.

(2) Cyclic quaternary ammonium salts of the imidazolinium type, for example di(hydrogenated tallow) dimethylimidazolinium dimethyl sulfate, 1-ethylene-bis(2-tallow-1-methyl)imidazolinium dimethyl sulfate and the like;

(3) Diamido quaternary ammonium salts, for example: methyl-bis(hydrogenated tallow amidoethyl)-2-hydroxyethylammonium dimethyl sulfate, methyl-bis(tallow amidoethyl)-2-hydroxypropylammonium dimethyl sulfate and the like;

(4) Biodegradable quaternary ammonium salts, such as N,N-di(tallow-oyl-oxy-ethyl)-N,N-dimethylammonium dimethyl sulfate and N,N-di(tallow-oyl-oxy-propyl)-N,N-dimethylammonium dimethyl sulfate. Biodegradable ammonium salts are described, for example, in U.S. Patent Specifications 4 137 180, 4 767 547 and 4 789 491 and are included herein by virtue of that literature reference.

Preferred biodegradable quaternary ammonium salts include the biodegradable cationic diester compounds, as are described in U.S. Patent Specification 4 137 180, and are included herein by virtue of that literature reference.

(ii) Tertiary fatty amines containing at least one, preferably two, C₈-C₆₀, preferably C₁₂-C₂₂-alkyl chains. Examples include hydrogenated tallow dimethylamine and cyclic amines such as 1-(hydrogenated tallow) amidoethyl-2-(hydrogenated tallow) imidazoline. Cyclic amines which can be used for the compositions herein are described in U.S. Patent Specification 4 806 255 and are included herein by virtue of that literature reference.

(iii) Carboxylic acids having from 8 to 30 carbon atoms and one carboxyl group per molecule. The alkyl moiety has from 8 to 30, preferably from 12 to 22, carbon atoms. The alkyl moiety may be linear or branched, saturated or unsaturated, with linear saturated alkyl being preferred. Stearic acid is a preferred fatty acid for use in the composition of this invention. Examples of such carboxylic acids are commercial grade stearic acid and palmitic acid and mixtures thereof, which may contain small amounts of other acids.

(iv) Esters of polyhydric alcohols, for example sorbitan esters or glycerin stearate. Sorbitan esters are the condensation products of sorbitol or isosorbitol with fatty acids, for example stearic acid. Preferred sorbitan esters are monoalkyl. A customary example of sorbitan esters is SPAN® 60 (ICI), a mixture of sorbitan and isosorbitol stearates.

(v) Fatty alcohols, ethoxylated fatty alcohols, alkylphenols, ethoxylated alkylphenols, ethoxylated fatty amines, ethoxylated monoglycerides and ethoxylated diglycerides.

(vi) Mineral oils and polyols, for example polyethylene glycol.

Those softeners are described in greater detail in U.S. Patent Specification 4 134 838, the disclosure of which is included herein by virtue of that literature reference. Preferred softeners for use in this invention are acyclic quaternary ammonium salts. It is also possible to use mixtures of the above-mentioned softeners.

The softener composition used in this invention preferably comprises from about 0.1 to about 95 % by weight of the T softener component, based on the total weight of the softener

composition. Preference is given to an amount of from 0.5 to 50 % by weight, especially an amount of from 2 to 50 % by weight and most especially an amount of from 2 to 30 % by weight.

The amount of cationic polymer in the softener composition is preferably from 0.005 to 15 % by weight, based on the total weight of the softener composition. Preference is given to an amount of from 0.01 to 10 % by weight, especially an amount of from 0.05 to 5 % by weight and most especially an amount of from 0.1 to 5 % by weight.

The softener composition may also comprise additives conventional for commercial softener compositions, for example alcohols, such as ethanol, n-propanol, isopropanol, polyhydric alcohols, for example glycerol and propylene glycol; amphoteric and non-ionic surfactants, for example carboxyl derivatives of imidazole, oxyethylated fatty alcohols, hydrogenated and ethoxylated castor oil, alkyl polyglycosides, for example decylpolyglucose and dodecylpolyglucose, fatty alcohols, fatty acid esters, fatty acids, ethoxylated fatty acid glycerides or fatty acid partial glycerides; also inorganic or organic salts, for example water-soluble potassium, sodium or magnesium salts, non-aqueous solvents, pH buffers, fragrances, dyes, hydrophobic agents, antifoams, greying inhibitors, enzymes, fluorescent whitening agents, anti-shrink agents, stain removers, germicides, fungicides, dye fixatives or dye transfer inhibitors (as described in WO-A-02/02865), antioxidants, corrosion inhibitors, wrinkle recovery agents or wet-soiling reducers, for example polyorganosiloxanes. The last two additives are described in WO0125385.

Such additives are preferably used in an amount of from 0 to 30 % by weight, based on the total weight of the softener composition. Preference is given to the use of an amount of from 0 to 20 % by weight, especially an amount of from 0 to 10 % by weight, and most especially an amount of from 0 to 5 % by weight.

The softener compositions are preferably in liquid aqueous form. The softener compositions preferably have a water content of from 25 to 90 % by weight, based on the total weight of the composition. The water content is especially from 50 to 90 % by weight, more especially from 60 to 90 % by weight.

The softener compositions preferably have a pH of from 2.0 to 9.0, especially a pH of from 2.0 to 5.0.

The softener compositions can be prepared, for example, as follows: An aqueous formulation of the cationic polymer is first prepared as described above. The softener composition according to the invention is usually, but not exclusively, prepared by first stirring the active ingredient, i.e. the hydrocarbon-based softener component, in molten form into water, following which further desired additives are added, if necessary, and lastly the formulation of the cationic polymer is added. The softener composition can also be prepared, for example, by mixing a pre-formulated softener with the cationic polymer.

Such softener compositions are conventionally prepared in the form of dispersions comprising, for example, up to 30 % by weight of active component in water. They usually have a cloudy appearance. It is, however, also possible to prepare alternative formulations, which normally comprise active ingredients in amounts of from 5 to 40 % by weight together with solvents, in the form of microemulsions which have a clear appearance (with regard to solvents and formulations see, for example, US-A 5 543 067 and WO-A 98/17757).

A very preferred softener composition according to the invention is in liquid form and comprises:

- A) from 0.5 to 50 % by weight, based on the total weight of the composition, of at least one softener component;
- B) from 0.005 to 15 % by weight, based on the total weight of the composition, of at least one thickener, especially a polymeric thickener;
- C) from 0.1 to 70 % by weight, based on the total weight of the composition, of granules comprising
 - a) from 1 to 90 % by weight, preferably from 5 to 88 % by weight, more preferably from 10 to 78 % by weight, of polydiallyldimethylammonium compounds, especially polydiallyldimethylammonium salts, bischloromethylbiphenylpolyquat compounds, the compound polyethyleneimine and basic polycondensation products, preferably those containing imidazolidine units and especially Tinofix CL[®],

- b) from 2 to 80 % by weight of at least one carrier from the group consisting of zeolites, bentonites, kieselguhr, talc, kaolin, mica, fuller's earth, cellulose, feldspar and condensation products of urea and formaldehyde,
 - c) from 0 to 60 % by weight of at least one non-ionic dispersant and/or water-soluble polymer from the group consisting of starch, maltodextrin and carboxymethylcellulose, hydroxymethylcellulose, polyethylene glycols, ethylene oxide/propylene oxide copolymers, polyvinyl alcohols and gelatin, and
 - d) from 0 to 20 % by weight of at least one further additive from the group consisting of wetting agents; disintegrators; fillers, water-insoluble or water-soluble dyes or pigments; dissolution accelerators; fluorescent whitening agents; aluminium silicates; powdered cellulose; fibrous cellulose; microcrystalline cellulose; talc; kaolin; TiO_2 ; SiO_2 and magnesium trisilicate, and
 - e) from 0 to 15 % by weight water, in each case based on the total weight of the granules,
- D) from 0 to 20 % by weight, based on the total weight of the composition, of at least one further conventional auxiliary substance, and
- E) water to 100 % by weight.

The softener compositions can also be used in the form of a sheet for use in a dryer. In such forms of application, the compositions are usually incorporated in impregnating agents on nonwoven sheets. However, other forms of application are also known.

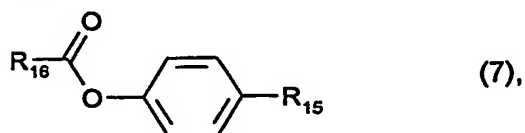
When the particulate composition is a constituent of a washing or softener composition, the content of dye fixative is, for example, in the range of from 0.1 to 70 % by weight, especially from 0.2 to 50 % by weight and preferably from 0.3 to 40 % by weight, based on the total weight of the washing or softener composition. For that purpose, preference is given to liquid washing and softener compositions.

According to a further embodiment, the fixative is used together with a bleaching agent. Suitable bleaching agents are solid bleaching agents. Thus, there come into consideration as peroxide component, for example, the commercially available organic and inorganic peroxides known from the literature, which bleach textile materials at customary washing temperatures, for example from 10 to 95°C.

The organic peroxides are, for example, mono- or poly-peroxides, especially organic peracids or salts thereof, such as phthalimidoperoxycaproic acid, peroxybenzoic acid, diperoxydodecanedioic acid, diperoxynonanedioic acid, diperoxydecanedioic acid, diperoxyphthalic acid or salts thereof.

Preference is given, however, to the use of inorganic peroxides, for example persulfates, perborates, percarbonates and/or persilicates. Of course, it is also possible to use mixtures of inorganic and/or organic peroxides. The peroxides may be present in various crystalline forms and may have different water contents and can also be used together with other inorganic or organic compounds in order to improve their storage stability.

Further bleach-activating substances are known transition metal salts or complexes and/or conventional bleach activators; that is to say compounds that, under perhydrolysis conditions, yield unsubstituted or substituted perbenzo- and/or peroxy-carboxylic acids having from 1 to 10 carbon atoms, especially from 2 to 4 carbon atoms. Also suitable are the customary bleach activators mentioned earlier that carry O- and/or N-acyl groups having the mentioned number of carbon atoms and/or unsubstituted or substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetythylenediamine (TAED), acylated glycolurils, especially tetraacetylglycoluril (TAGU), N,N-diacetyl-N,N-dimethylurea (DDU), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), and compounds of formula (7)



wherein

R_{15} is a sulfonate group, a carboxylic acid group or a carboxylate group, and R_{16} is linear or branched ($\text{C}_7\text{--C}_{15}$)alkyl.

Also suitable are activators known under the names SNOBS, SLOBS and DOBA, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran and acetylated sorbitol and mannitol and acylated sugar derivatives, especially pentaacetylglucose (PAG), sucrose polyacetate (SUPA), pentaacetylfructose, tetraacetylxylose and octaacetylactose and acetylated, optionally N-alkylated glucamine and gluconolactone. It is also possible to use the combinations of conventional bleach activators

known from German Patent Application DE-A-44 43 177. There also come into consideration as bleach activators nitrile compounds that form periminic acids with peroxides. Mention may also be made of sodium hypochlorite, Javelle water and hydrogen peroxide.

The bleaching agents are preferably used as a further constituent of the liquid, aqueous dye fixative formulations given above. The definitions and preferred meanings given above apply also to those aqueous, liquid formulations. The definitions and preferred meanings given above apply also to the dye fixatives. Of special interest are dye fixatives of formula(1) that have been neutralised wholly or partially with acetic acid. The concentration of the bleaching agents can vary within a wide range and is preferably from 0.1 to 25 % by weight, especially from 0.5 to 20 % by weight and preferably from 0.5 to 10 % by weight, based on the total weight of the formulation. Preference is given to a lower limit of 1 % by weight, especially 2 % by weight.

In addition, it is of course also possible for the bleaching agent and the dye fixative to be applied separately. Applications that come into consideration are those mentioned above. Thus, application can be effected, for example, before the washing procedure, during or after the washing procedure, preferably during the washing procedure.

The bleach-containing dye fixative is preferably not a constituent of a washing or softener composition.

Textile fibre materials that come into consideration are, for example, hydroxy-group-containing and amino-group-containing fibre materials. Examples that may be mentioned are polyamide, wool and especially natural or regenerated cellulose.

The materials treated according to the method of the invention exhibit markedly reduced dye transfer to other materials, for example materials that are undyed or are dyed in different or pale shades, that effect being almost entirely retained without renewed treatment even after several washes. The colour shade of the dyed materials is also retained to a great extent even after several washes. The particulate compositions can be formulated with the addition of surfactants without reducing the activity profile of the dye fixatives; especially for treatment before or after washing. The particulate compositions can also be combined surprisingly well with bleaching agents, thereby enabling them to be applied together with bleaching agents. The dye fixatives can also be combined very well with commercially available washing compositions.

The following Examples illustrate the invention. Parts denote parts by weight, unless otherwise indicated. The temperature is in degrees Celsius, unless otherwise indicated.

Example 1:

2000 g of an aqueous solution (dry material content = 35%) of the active ingredient in the form of the dye fixative Tinofix CL[®] are introduced into a 10 000 ml container and diluted with 3500 g of deionised water. 220 g of the maltodextrin Glucidex 15D[®] (Roquette, France) are dissolved completely, with stirring, in the resulting solution. 1210 g of zeolite (Wessalith XD[®], Degussa AG, Germany) are then suspended in the aqueous solution and homogenisation is carried out with stirring for 2 hours. The suspension having a solids content of 30.7% is then filtered through a 50 µm screen and then granulated in a bench-scale fluidized spray dryer (FSD). In the first phase of the granulation process, the seeds are built up in the fluidised bed ($T_{\text{inlet air}} = 190^{\circ}\text{C}$, $T_{\text{bed}} = 102^{\circ}\text{C}$, $T_{\text{exhaust air}} = 110^{\circ}\text{C}$). When enough seeds are present in the fluidised bed for granulation, the exhaust air temperature is lowered in order to initiate the granulation process. Granulation of the entire suspension is carried out at an exhaust air temperature of 62°C and a fluidised bed temperature of 65°C . The product at the outlet of the granulator contains about 11 % by weight residual moisture and is then dried to the desired value of 5 % by weight in a vacuum cabinet at 90°C and 200 mbar. The finished granules contain 31.2 % of the dye-fixing active ingredient and are from 50 to 310 µm in size, having a bulk density of 650 g/litre. The granules can be incorporated directly into a solid washing composition.

Example 2:

An aqueous suspension having the same composition as in Example 1 is prepared and is spray-granulated in a laboratory spray tower instead of in the FSD.

Spray parameters: $T_{\text{inlet air}} = 220^{\circ}\text{C}$, $T_{\text{exhaust air}} = 102^{\circ}\text{C}$. Flowable granules having a mean particle size of 65 µm, a bulk weight of 380 g/litre and a residual water content of 6.0 % are obtained. The granules prepared in that manner contain 30.9 % of the dye fixative.

Examples 3 to 5:

According to the process described in Example 1, in Examples 3 to 5 there are prepared granules having the following composition (the percentages in each case denoting percent by weight, based on the total weight of the composition):

In Example 3:

dye fixative: 25 % by weight of active ingredient analogous to Example 1,
carrier: 49 % by weight of zeolite (Na-Al silicate) (Advera 401 P®, PQ Corp.),
binders: 2 % by weight of the sodium salt of polymerised alkylnaphthalene
sulfonic acid,
12 % by weight of maltodextrin (Glucidex 15D®, Roquette, France),
5 % by weight of carboxymethylcellulose (Blanose 7ULC®, Aqualon,
France),
residual moisture: 7 % by weight.

In Example 4:

dye fixative: 30 % by weight of active ingredient analogous to Example 1,
carrier: 58 % by weight of cellulose fibres (Arbocel FDY600®, J.
Rettenmaier&Söhne, Germany),
5 % by weight of dextrin,
binders: 2 % by weight of polyethylene glycol 8000,
1 % by weight of gelatin,
residual moisture: 4 % by weight.

In Example 5:

dye fixative: 40 % by weight of active ingredient analogous to Example 1,
carrier: 52 % by weight of Wessalith XD®,
residual moisture: 8 % by weight.

Example 6:

950 g of a solution of the active ingredient in the form of the dye fixative Tinofix CL® (35 % solids content) are introduced into a glass beaker, and 60 g of polyethylene glycol 8000 and 110 g of maltodextrin (Glucidex 12D®) are completely dissolved, in succession, in that solution with stirring. The finished homogenised dye fixative solution is used as granulating solution.

400 g of zeolite (Wessalith XD®) are introduced into a laboratory fluidised bed granulator (STREA-1®; Aeromatic AG, Bubendorf, Switzerland). The temperature of the air flowing into the bed is set at 63°C. When the temperature of the zeolite introduced into the fluidised bed has reached 63°C, spraying of the granulating solution onto the zeolite commences. Granulation continues until all the granulating solution has been sprayed in. The granules are

then dried in the bed for 1 hour at 63°C and subsequently cooled in the fluidised bed in a cold air stream (20°C). The granules have a mean particle size of 480 µm, a residual moisture content of 5.1% and a bulk weight of 720g/litre. The granules contain 35 % dye-fixing active ingredient.

Example 7:

1270 g of a condensation product of urea and formaldehyde in powder form (Tino Flow P®) are introduced into a 5 litre horizontal mixer (ploughshare mixer, made by Lödige). The mixer is switched on and the speed is set at 350 rpm. 1343 g of granulating liquid are slowly sprayed into the mixer (over a period of 60 min). The granulating solution was prepared from 1143 g of Tinofix CL® (dry material content = 35 %), in which there have been dissolved, in succession, 40 g of polyvinyl alcohol (Mowiol3-83®) and 160 g of dextrin.

When granulation has ended, the wet granules are discharged from the mixer into a laboratory fluidised bed and then dried in an air stream at a temperature of 80°C until the residual water content is 6.5 %, yielding granules containing 20 % dye fixative and having a particle size of 380 µm and a bulk weight of 630 g/litre.

Example 8:

20 g of carboxymethylcellulose, 20 g of the sodium salt of polymerised alkylnaphthalene-sulfonic acid and 150 g of the maltodextrin Glucidex 19D® are dissolved, in succession, in 629 g of liquid Tinofix CL® (dry material content 35 %) in a glass beaker. In a laboratory kneading apparatus the solution is kneaded together with 550 g of the zeolite CBV 901® to form a homogeneous paste. The paste is then extruded using a laboratory extruder. The extruded material has a diameter of 1 mm and an average length of 2 mm. The wet extruded material is then dried to a residual moisture content of 3.5 % in a vacuum cabinet. The dry product contains 22 % of the dye fixative.

Example 9:

600 g of cellulose fibres (Arbocel BC200®) are suspended in 1333 g of Tinofix CL® solution (dry material content = 35 %). The suspension is dried in a laboratory paddle dryer *in vacuo* (80 mTorr) at 120°C for 24 hours. The dry residue is then ground. The ground material is kneaded in a kneading machine together with a mixture of 125 g of an ethylene oxide/-propylene oxide copolymer (MW = 8500; melting point = 55°C) and 125 g of a non-ionic surfactant (C₁₈ alcohol ethoxylate containing 80 EO units; melting point = 56°C) and then

extruded in a heatable extruder at 56°C. The extruded material has a diameter of 0.8 mm and is 1.5 mm long and is solidified on a cooling belt. The extruded material so produced contains 35.5 % of the dye fixative and has a bulk weight of 810 g/litre.

Example 10:

A mixture of 750 g of the zeolite Wessalith XD® and 2143 g of liquid Tinofix CL® (dry material content = 35 %) is dried and ground as described in Example 9. The dry mixture is introduced into a laboratory fluidised bed granulator (STREA-1®; Aeromatic AG, Bubendorf, Switzerland) and then granulated with a separately prepared granulating solution at a bed temperature of 80°C. The granulating solution is composed of 26.4 g of gelatine and 158.2g of dextrin dissolved in 734 g of deionised water. At the end of the granulation, the granules are dried to a residual moisture content of 4.2 % in the same fluidised bed. The dye fixative content in the finished granules is 42.6 %. The granules are on average 500 µm in size and have a bulk weight of 780 g/litre.

Example 11:

700 g of bentonite Laundrosil DGA® are suspended in 1429 g of liquid Tinofix CL® (dry material content = 35 %). The suspension is dried and ground as described in Example 9. The dry bentonite/dye fixative mixture is introduced into a 5 litre horizontal mixer (ploughshare mixer, made by Lödige). The mixer and its contents are adjusted to a temperature of 55°C. 263 g of polyethylene glycol 8000 and 87 g of non-ionic surfactant (C₁₈ alcohol ethoxylate containing 25 EO units having a melting point of 47°C) are melted separately. The two molten components are mixed together and then adjusted to a temperature of 75°C. The melt is then metered into the ploughshare mixer through a unitary nozzle, the speed of the mixer being set at 330 rpm. When the metering in is complete, the temperature of the mixer is lowered gradually to 40°C. At 30°C the solidified granules are removed from the mixer. The granules contain 32 % of the dye fixative and are on average 520 µm in size.

Example 12:

430 g of cellulose granules (Arbocel G350®) and 58 g of calcium carbonate are introduced into 630 g of an aqueous solution of the active ingredient in the form of the dye fixative Tinofix CL® having a dry material content of 33.2 %. The mixture is dried *in vacuo* in a laboratory paddle dryer as described in Example 9, and the residue is ground. The resulting

material is then granulated in a laboratory fluidised bed granulator (STREA-1®; Aeromatic AG, Bubendorf) together with 450 g of a 20 % aqueous maltodextrin solution (Glucidex 12D®) as granulating solution at a fluidised bed temperature of 75°C. The resulting product is then dried at that temperature to a residual moisture content of 6 % and then cooled to room temperature in a stream of cold air. The resulting granules have a mean particle size of 660 µm with a bulk weight of 610 g/litre and contain 25 % fixative.

Example 13:

Following up the process described in Example 7, the granules, during drying, are sprayed in a second step with a 20 % aqueous solution of a polyethylene oxide/polypropylene oxide block copolymer having 80 % polyethylene in the molecule, until a content of 5 % of the coating material on the core granules is reached. The coated granules are dried in the fluidised bed to a residual moisture content of 7 % and have a fixative content of 19 % with a mean particle size of 420 µm.

Example 14:

After-treatment is carried out analogously to Example 13 by spraying with a heated 10 % aqueous solution of a partially hydrolysed polyvinyl alcohol having a molecular weight of about 15 000 g/mol, until the amount of coating material on the resulting granules is 5 %. Drying to a residual moisture content of 8 % yields free-flowing granules having a dye fixative content of 19 % and a mean particle size of 450 µm.

Example 15:

In a modification to the process described in Example 13, the granules from the fluidised bed are discharged at 75°C into a Lödige ploughshare mixer. At the rated speed of rotation of the mixer, there is metered in, in the course of 60 seconds, sufficient PEG 8000 melt, preheated to 80 to 90°C, to provide 5 % of the coating material on the granules. Stirring is then carried out for about 3 to 4 minutes in order to achieve homogeneous distribution of the melt in the mixture, and the mixture is discharged into a fluidised bed for cooling. The resulting granules contain 19 % of the dye fixative and have a mean particle size of 410 µm.

Application Examples

Example 16:

This Example illustrates the use of the dye fixative formulations in washing compositions and in the washing of textile materials:

The following washing formulations are prepared:

Washing composition no. 1: ECE 98 standard washing composition containing 4 % TINOFIX
CL AS incorporated *via* slurring

Washing composition no. 2: ECE standard washing composition

Washing composition no. 3: 3.2 % by weight dye fixative granules from Example 1

Washing composition no. 4: 6.4 % by weight dye fixative granules from Example 1

Washing composition no. 5: 12.8 % by weight dye fixative granules from Example 1

Washing composition no. 6: 2.8 % by weight dye fixative granules from Example 9

Washing composition no. 7: 5.6 % by weight dye fixative granules from Example 9

Washing composition no. 8: 11.2 % by weight dye fixative granules from Example 9

5 g of cotton fabric dyed with D Blue (2.09 %) (bleeder fabric) are washed with 5 g of bleached undyed cotton fabric (accompanying fabric) under the following conditions.

washing composition concentration : 2.5 g/litre

liquor ratio : 1:10

temperature : 40°C

duration : 15 minutes

The fabrics are then rinsed for 30 seconds under running tap water, spun and dried.

The undyed cloth is removed and replaced by a fresh piece of accompanying fabric, and the wash is repeated, as described above, a further 4 times with the same dyed fabric but in each case a new accompanying fabric.

Evaluation:

The extinction of the wash bath was determined at 600 nm (after centrifugation to remove the zeolite).

The Delta E of each accompanying fabric compared with the starting material was determined.

Table 1:

| Washing composition no.: | Extinction of the wash liquor | | Delta E of the accompanying fabric | |
|--------------------------|-------------------------------|----------------|------------------------------------|----------------|
| | after 3rd wash | after 5th wash | after 3rd wash | after 5th wash |
| 1 | 0.25 | 0.20 | 27 | 24 |
| 2 | 0.123 | 0.138 | 25 | 24 |
| 3 | 0.135 | 0.195 | 19 | 19 |
| 4 | 0.241 | 0.232 | 16 | 15 |
| 5 | 0.271 | 0.257 | 12 | 10 |
| 6 | 0.246 | 0.163 | 19 | 18 |
| 7 | 0.170 | 0.164 | 18 | 15 |
| 8 | 0.27 | 0.192 | 9 | 9 |

The tests demonstrate a colour-protecting effect for the accompanying fabric when using washing formulations nos. 3-8.

Example 17

The blue fabrics of tests 1-8 are each washed again after the 5th wash with a fresh accompanying fabric under the conditions already mentioned.

The washing composition now used for all the pieces of fabric is ECE 77 without any additives. Any possible fixative effect would emerge here most clearly, and can only be caused by the product already present on the textile.

Evaluation:

The extinction of the wash bath was determined at 600 nm.

The Delta E of each accompanying fabric compared with the starting material was determined.

Table 2:

| Washing composition no.: | Extinction of the wash liquor | | Delta E of the accompanying fabric | |
|--------------------------|-------------------------------|----------------|------------------------------------|----------------|
| | after 6th wash | after 7th wash | after 6th wash | after 7th wash |
| 1 | 0.073 | 0.060 | 19 | 19 |
| 2 | 0.043 | 0.035 | 20 | 21 |
| 3 | 0.028 | 0.021 | 15 | 18 |
| 4 | 0.020 | 0.012 | 11 | 15 |
| 5 | 0.030 | 0.003 | 7 | 10 |
| 6 | 0.021 | 0.016 | 13 | 17 |
| 7 | 0.026 | 0.011 | 11 | 15 |
| 8 | 0.023 | 0.002 | 7 | 9 |

The results in Table 2 clearly show that, as a result of the fixative action of formulations nos. 3-8, both bleeding of the dye into the washing liquor and staining of the accompanying material are less than when reference washing compositions no. 1 and no. 2 are used.